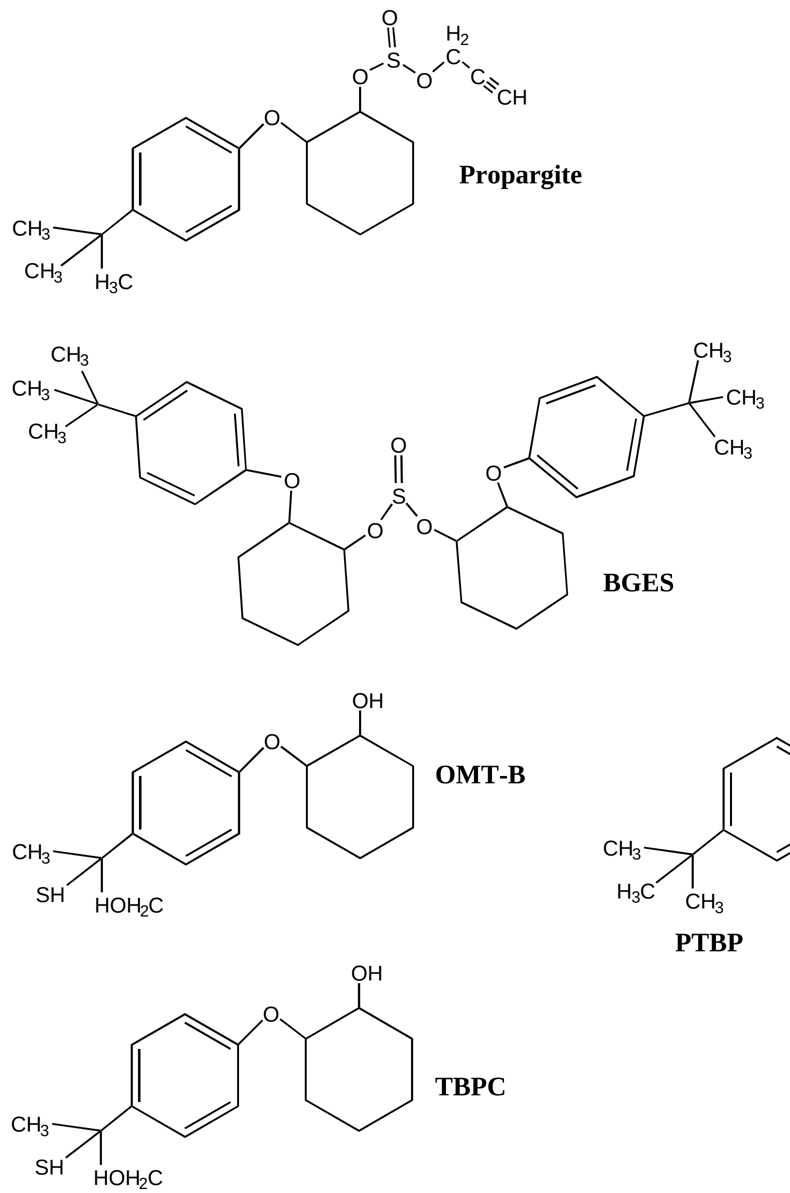
Appendix B. Supplemental Fate Information for Propargite

Propargaite and Degradate Chemical Structures

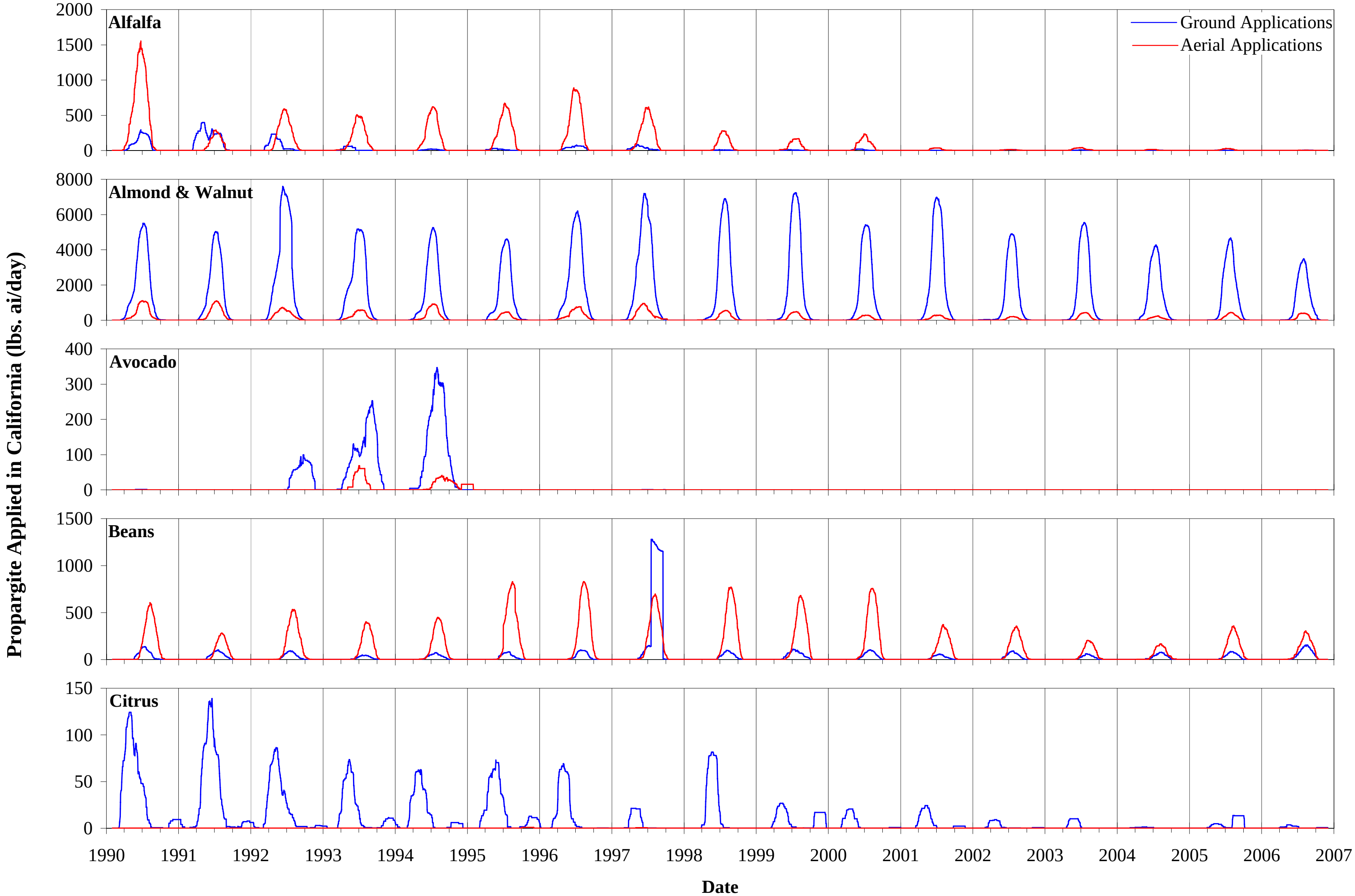
Chemical structure diagrams for propargite and four of its degradates identified in fate studies are shown in Appendix Figure B1. Discussion of degradates occurs in Section 2.2 of the main document. Maximum degradate yields from each fate study are included in Table 2.1 of the main document.



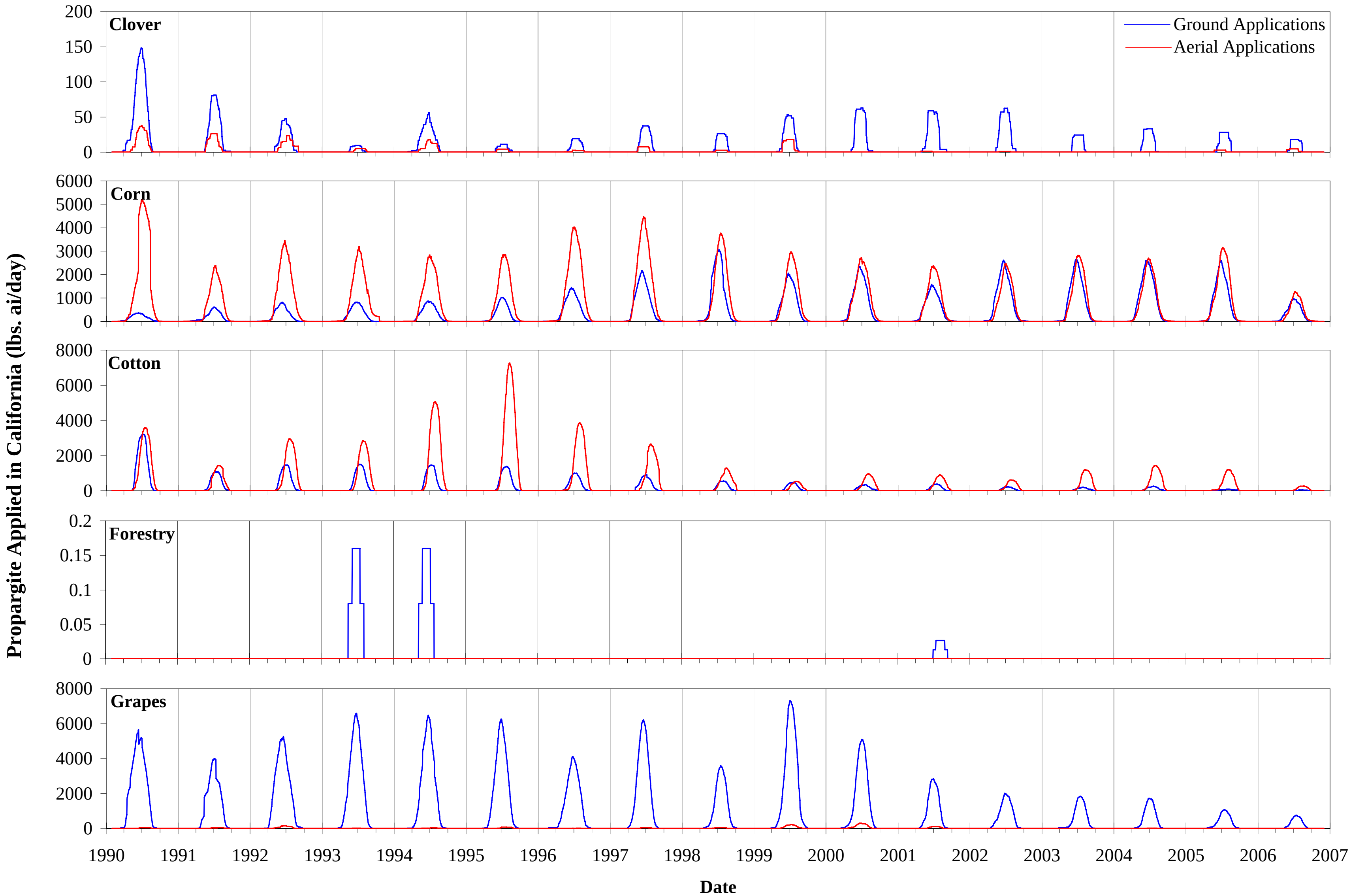
Appendix Figure B1. Propargite and degradate chemical structures as discussed in Section 2.2 of the main document.

Historical Propargite Use

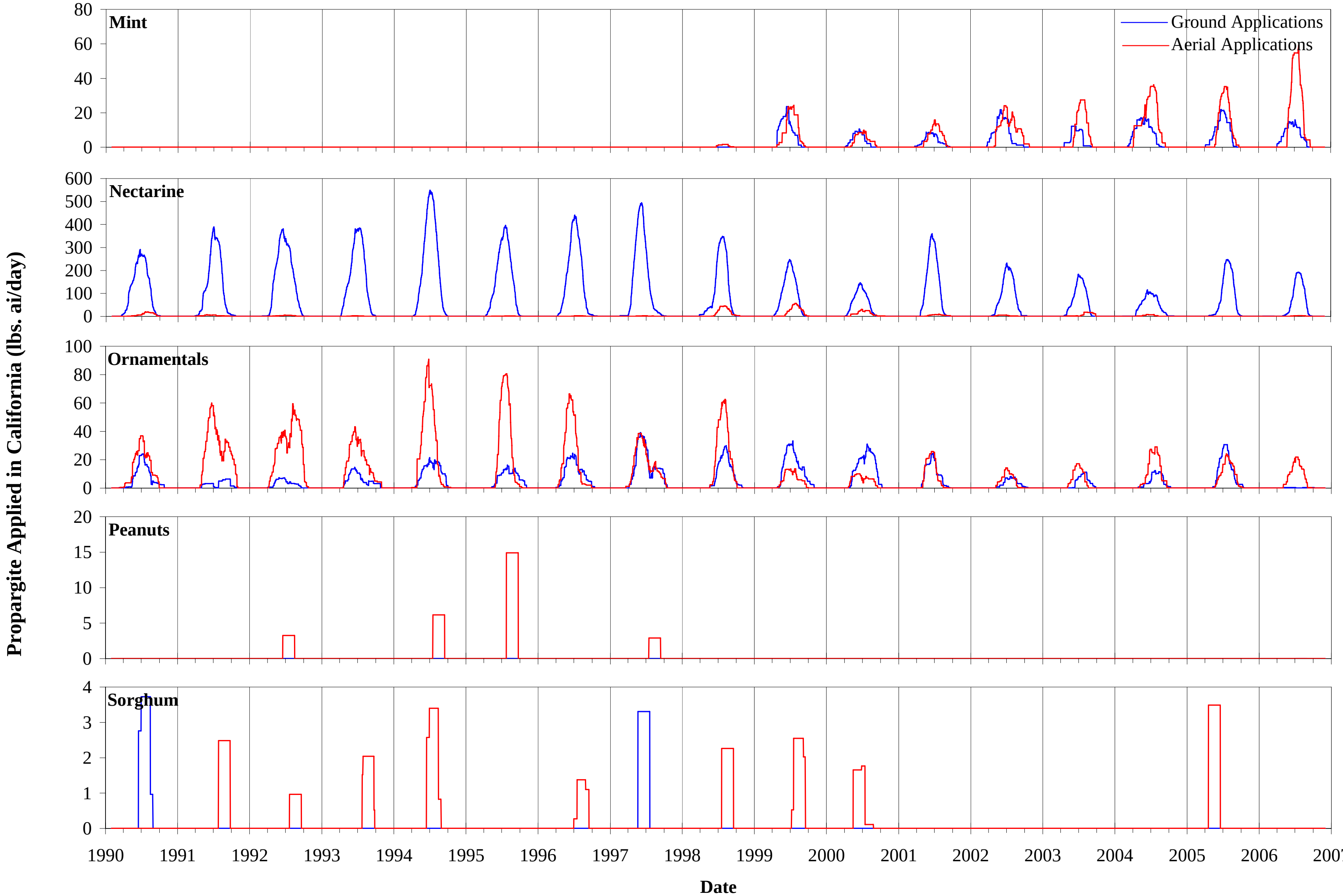
Information on the historical usage of propargite in California was obtained California Department of Pesticide's Pesticide Use Reporting (CDPR PUR) data set. The full CDPR PUR data set contains pesticide use data from 1990 through 2006. This data is summarized in the following graph (Appendix Figure B1). For each exposure scenario group, trends in propargite application (lbs/day) were obtained using moving averages. Inter-year variation in propargite application are depicted using a 60-day moving average for CDPR PUR data from 1990-2006. This graph provides some indication of whether intra-annual temporal trends in propargite applications are consistent between years and how propargite usage has changed across years.



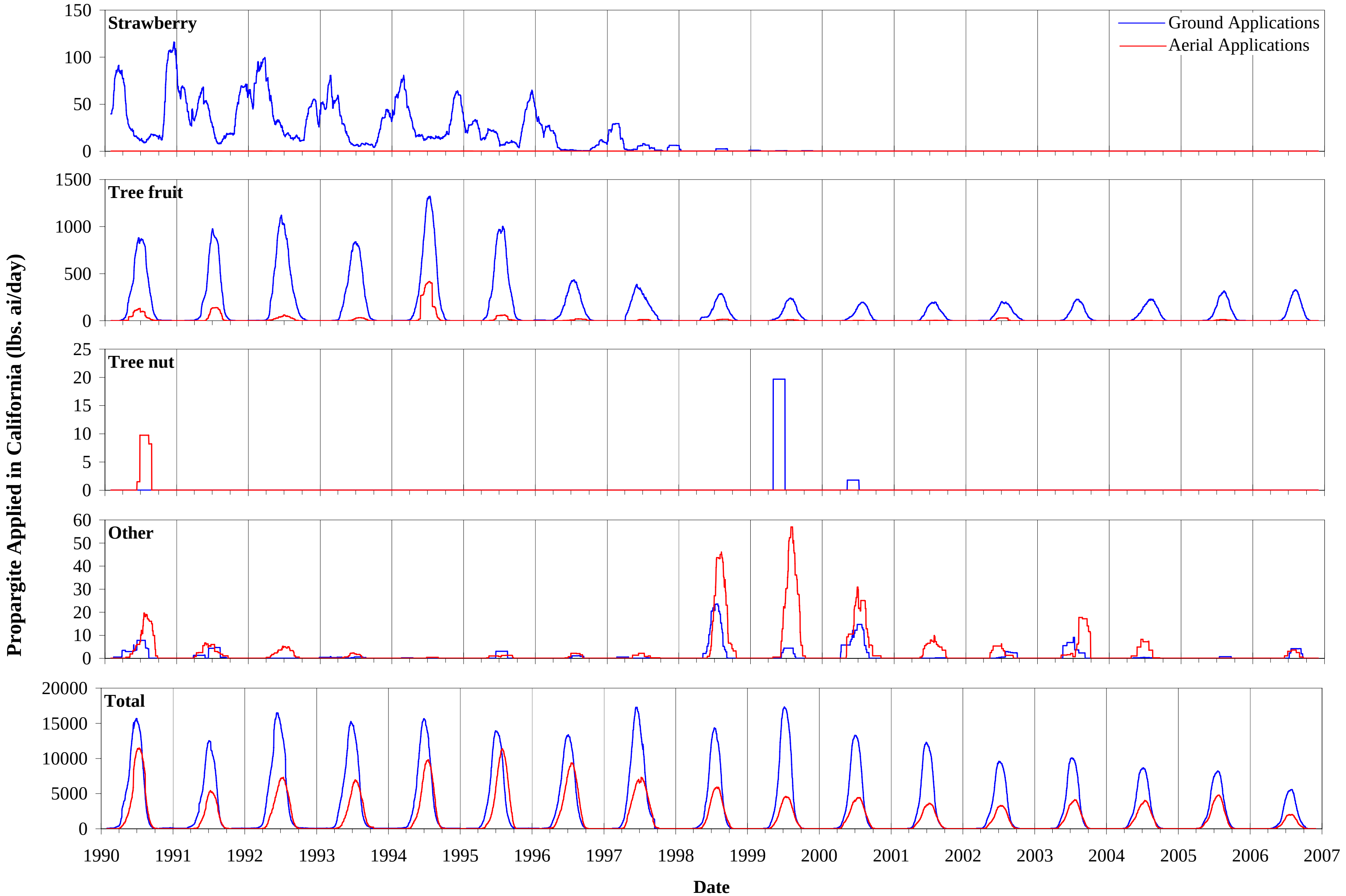
Appendix Figure B2. Variation in the rate of propargite application from 1990 through 2005 in California by use (other uses recorded in the CDPR PUR data set include barley, broccoli, cantaloupe, carrots, commodity fumigation, cucumber (pickling, chinese, etc.), forage - fodder grasses…



Appendix Figure B2. Continued …melons, melons, nursery-greenhouse grown cut flowers or greens/plants in containers/transplant/propagative material, oats, pastures, peas, pumpkin, regulatory pest control, research commodity, rice, rights of way, safflower, site unknown, soil application…



Appendix Figure B2. Continued …preplant-outdoor (seedbeds, etc.), soybeans, structural pest control, sudangrass, sugarbeet, tomatoes, uncultivated agricultural areas, vetch, watermelons, and wheat).



Appendix Figure B2. Continued.

Fate Properties

Hydrolysis

Propargite hydrolyzes rapidly under alkaline (pH 9 half-life = 2.2 days), slowly under neutral (half-life = 75 days) and is stable in acidic conditions (pH 5 half-life = 120 days). Propargite glycol ether (TBPC, see Appendices for structure), the alcohol glycol ether hydrolysis product of propargite, was the major degradate detected which was present at maximum concentrations of 7.8, 37, and 88% of applied in the pH 5, 7 and 9 studies, respectively (MRID 40358401)

Aqueous Photolysis

Aqueous photolysis does not appear to be a significant mode of degradation since there were little differences between light exposed and non-exposed samples. Aqueous photolysis half-lives of 134 and 140 days were reported for propargite when pH 5 buffered test solutions were exposed to a xenon arc lamp light source. TBPC and PTBP at maximum concentrations of 7.3 and 13 %, respectively, were the only reported photolysis degradates detected in the study (MRID 40354802)

Soil Photolysis

Soil photolysis does not appear to be a significant route of dissipation for propargite. Propargite degraded with registrant calculated half-lives (dark control corrected) of 63 days (12 hours light/12 hours dark) on sterilized sandy clay loam soil (pH 6.9) and 91 days on unsterilized sandy loam soil that was exposed to a continuous light source at 25 ^oC. The half-life in the dark control was 113 days. TBPC reached a maximum concentration of 20.8% of applied radioactivity in the light exposed test samples and a maximum of 15.6% of applied in the dark control test samples during the study. Soil bound residues reached a maximum concentration of 6.3% and volatile compounds were <1% of applied radioactivity (MRIDs 40358402, 42319301, and 42319307)

Aerobic Soil Metabolism

Radiolabelled propargite, at 6.0 μg/g, had a first order half-life of 168 days (r^2=0.92) in a sandy loam soil (pH=6.6) when incubated under aerobic conditions at 25°C. The study authors reported biphasic degradation curves. The initial rapid half-life (0 to 59 days post-treatment) was 67 days (R^2 = 0.98) and the second phase (59 to 365 days post-treatment) half-life was approximately 231 days (R^2 = 0.99). However, EFED believes that linear regression of time vs. natural logarithm of concentration, which is EFED's conventional method of determining a half-life, adequately describes the degradation kinetics of propargite in aerobic soil.

Nine metabolites were detected during the testing period. Metabolites identified were the sulfate derivative of TBPC (MET-8, maximum concentration of 7.62% of applied) and TBPC (MET-3, maximum concentration of 1.98% of applied, see Appendices for structure). Carbon dioxide was detected at a maximum concentration of 32% of the applied radioactivity by the end of the study. Seven metabolites were detected in concentrations <0.65% of applied radioactivity. In addition, soil-bound radio-labeled residues (32.96% of applied radioactivity) were detected in soil organic matter (SOM) fractions. Propargite and TBPC were identified in SOM extracts in concentrations of 1.47 and 1.57% of applied radioactivity, respectively (MRID 43851402)

Anaerobic Soil Metabolism

Anaerobic soil metabolism does not appear to be a significant degradation pathway for propargite. The half-life of propargite, incubated anaerobically for 60 days, was 64.4 days (r^2=0.99) in the pH 6.9 sandy clay loam soil used. TBPC was detected in soil and water extracts at maximum concentrations of 20.3 and 3.4% of applied radioactivity, respectively. PTBP was only detected in the water phase at a maximum concentration 0.7% applied radioactivity. Soil bound residues and CO_2 were at maximum concentrations of 14.9% and 2.7% of applied radioactivity (MRID 41003602)

Anaerobic Aquatic Metabolism

Propargite degraded with a half-life of approximately 46.6 days (r^2=0.93) for the whole system (80.6 days in water fraction and 47.0 days in sediment) in flooded sand hydro-soil that was incubated in the dark at 25^{o}C under anaerobic conditions. Four degradates were identified: TBPC, 61.5%, (M1), PTBP, 1.57%, (M2), OMT-B, 2-[4-(1,1-dimethyl-2-hydroxyethyl)phenoxy] cyclohexane-1-ol, 4.7%, (M3), and BGES, bis-[2,-(4-(1,1-dimethyl-ethyl)-phenoxy)cyclohexyl]sulfite, 1.72%, (M8), Appendix 1). No other degradates were identified in the study. Only TBPC (61.5%) and OMT-B (4.7%) exceeded 2% of the applied in either the soil or aqueous phase. On day 270, TBPC reached a maximum 40.1% of the applied and OMT-B a maximum 4.1% of the applied test material in the aqueous phase; while in the soil phase, TBPC was 29.9%. Up to 5.14% of the applied was mineralized to CO_2 by 365 days, while approximately 25% became soil bound residues (MRID 43139401).

Aerobic Aquatic Metabolism

Propargite degraded with a half-life of approximately 38 days (r^2=0.98) in flooded loam lake sediment (pH 5.5) that was incubated in the dark at 25^{o}C under aerobic conditions. Four degradates were identified: TBPC, PTBP, OMT-B [2,2-dimethyl-2-(4'-(2-hydroxy-cyclohexoxy)phenyl)ethanol], and TBPC-Acid (2-[4-(2-hydroxycyclohexoxy)phenyl]-2,2-dimethyl acetic acid). TBPC was detected at a maximum concentration of 27.7%; while the other degradates were detected at concentrations $\leq$1.54% of the applied radioactivity. While most of the applied radioactivity persisted as parent in the soil, degradates dominated the aqueous phase by 14 days post-treatment. At 30 days, unextracted residues and volatile compounds totaled 4.8 and 0.68% of applied radioactivity, respectively (MRID 42688801).

Mobility

In two separate batch equilibrium studies, propargite was immobile and propargite glycol ether (TBPC), the primary degradate of propargite, was determined to be mobile to very mobile in the six soils from California, Connecticut, Maryland, Mississippi, and Florida used in the batch equilibrium studies. The organic carbon partitioning coefficients (K_{oc}s) and K_ds for parent ranged from 2963 to 57,966 mL/g and 60-218 mL/g, respectively, for the soils tested; while K_{oc}s and K_ds for TBPC ranged from 187-460 mL/g and 0.65-8.39 mL/g, respectively (see Appendix Table B1 below for details) (MRIDs 42908401 and 4298402)

Appendix Table B1. Results of batch equilibrium study to estimate leaching of propargite residues .

Soil Location	Soil Texture	Propargite		TBPC	
		Kd-mL/g	Koc-mL/g	Kd-mL/g	Koc-mL/g
California	sandy loam	107	25,918	1.17	284
Connecticut	loamy sand	92	2963	0.66	187
Maryland	sand	205	57,966	0.65	551
Mississippi	clay	218	11,929	6.7	215
Florida	sand	128	36,205	1.47	418
Florida	sand sediment	60	50,660	8..39	460

Terrestrial Field Dissipation

Five field dissipation studies were conducted on bare ground plots in California, and citrus and cotton plots in California and Florida using either emulsifiable concentrate, wettable powder, or a controlled release formulation of propargite applied 2 or 3 times at application rates ranging from 0.83 to 5.15 lb ai/A. Field dissipation half-lives were 67, 78, 87, 94, and 99 days.

In two acceptable studies conducted on citrus in Florida and California, propargite dissipated with half-lives of 67 and 87 days, respectively. In the Florida study, propargite was detected at a maximum concentration of 0.56 ppm in the 0-6 inch depth and decreased to $\leq$0.05 ppm by 151 days. Parent was not detected in any soil sample below the 0-6 inch depth. TBPC was <0.01 ppm (detection limit) in the soil at all depths and sampling intervals. In the California study, propargite was detected at a maximum concentration of 1.25 ppm in the 0-6 inch soil depth and decreased to $\leq$0.05 ppm by 190 days. Propargite was detected once in the 6-12-inch depth at 7 days (0.025 ppm), and was not detected in the 12-24 inch depth at any sampling interval. TBPC was detected at 0.019 to 0.113 ppm in the 0-6 inch depth in some of the replicates, but was not detected at any other soil depth (MRIDs 41307301 and 41731501).

In one acceptable study conducted on cotton in California, propargite dissipated with a half-life of 94 days. Propargite was at a maximum of 0.54 ppm in the 0-6 inch depth and then decreased to $\leq$0.05 ppm by 283 days. TBPC was <0.10 ppm (detection limit) in the soil at all depths and sampling intervals, except one soil sample in the 0-6 inch depth that contained 0.10 ppm at 91 days (MRID 41325901).

In two acceptable studies conducted on bareground plots in California, propargite dissipated with half-lives of 78 and 99 days, respectively, in sandy clay loam and loamy sand soils. At the two sites, propargite was at a maximum concentration in the 0-6 inch soil depth of 2.2 and 5.3 ppm after the second application and then decreased to 0.14 ppm by 354 days. Propargite was not detected in any other soil depth at any sampling interval at concentrations $\geq$0.05 ppm. The degradate TBPC varied in concentration from a maximum of 0.30 to 0.35 ppm to 0.016 ppm by day 354, with no distinct pattern of formation or decline. TBPC was generally not detected (at concentrations $\geq$0.10 ppm) in soil samples collected below the 0-6 inch depth, except in one sample from both the 6-12 and 12-24 inch depth that contained 0.16 and 0.10 ppm, respectively, immediately and 73 days after application. (MRID 40969501)

In all of the studies, factors contributing to the route of dissipation were never fully identified, but may include the degree of soil binding and subsequent runoff, and how favorable conditions were for microbial growth. These studies provide terrestrial dissipation information about a variety of soils.

Non-Guideline Terrestrial Field Runoff and Spray Drift Monitoring Studies

Measured residue levels from six monitoring studies indicate that propargite may drift and runoff in relatively large quantities under the conditions that existed during the time the studies were conducted. A total of six terrestrial field runoff monitoring studies were conducted on corn (Missouri, Texas), cotton (two in Georgia), and oranges (two in Florida). The studies were situated so that the crops (5.3 to 52 acres) were planted around irrigation ponds ranging from 0.43 to 3 acres so that any runoff (monitored by determining propargite concentration in pond water and/or in runoff water occurring after irrigation or rain) or spray drift (monitored with drift cards) that occurred was carried to the ponds. Total propargite applications ranged from 1.64 to 5.0 lb ai/A and were applied aerially.

Spray drift card analysis showed that significant amounts of applied propargite residues reached the pond waters through drift. The studies were conducted to allow spray drift to reach the ponds in order to measure the dissipation of propargite from pond water and sediment. Pond water showed propargite residues ranging in concentrations from <5.0 to 120 ug/L (ug/L); while the degradate TBPC was present at maximum concentrations of <5 to 63 ug/L. Propargite concentrations in the pond sediments ranged from <25 to 930 ug/L; while TBPC concentrations ranged from <25 to 72 ug/L. In all the studies, any propargite or TBPC reaching the pond was below the detection limit within 2 or 3 weeks after the final application. Runoff water collected at various locations in the fields after runoff events showed maximum propargite concentrations ranging from 18 to 269 ug/L, while TBPC concentrations ranged from 24 to 77 ug/L. However, no residues in runoff water above the detection limit were found in samples collected 1 month or more after the final application. Because of the variation in data, no half-lives could be calculated.

These studies provide supplemental data related to runoff and spray drift of propargite into farm ponds (MRID 40969501, 41057402, 41057401, 41153201, 41153205, 41225601, 41184001, and 41663201).

Bioconcentration

In a study conducted with bluegill sunfish (*Lepomis macrochirus*) at a concentration of 3.1 ug/L propargite for 35 days, bioconcentration factors were 260X for fillet, 1550X for viscera, and 775X for whole fish tissues. A steady state of bioaccumulation was reached after approximately 10 days of exposure. Depuration was relatively rapid, with 82% of the accumulated radioactive residues eliminated after 14 days in non-treated water.

Based on these data, propargite does not appear to bioaccumulate significantly in fish (MRIDs 40494801 and 40916601).

Application Timing

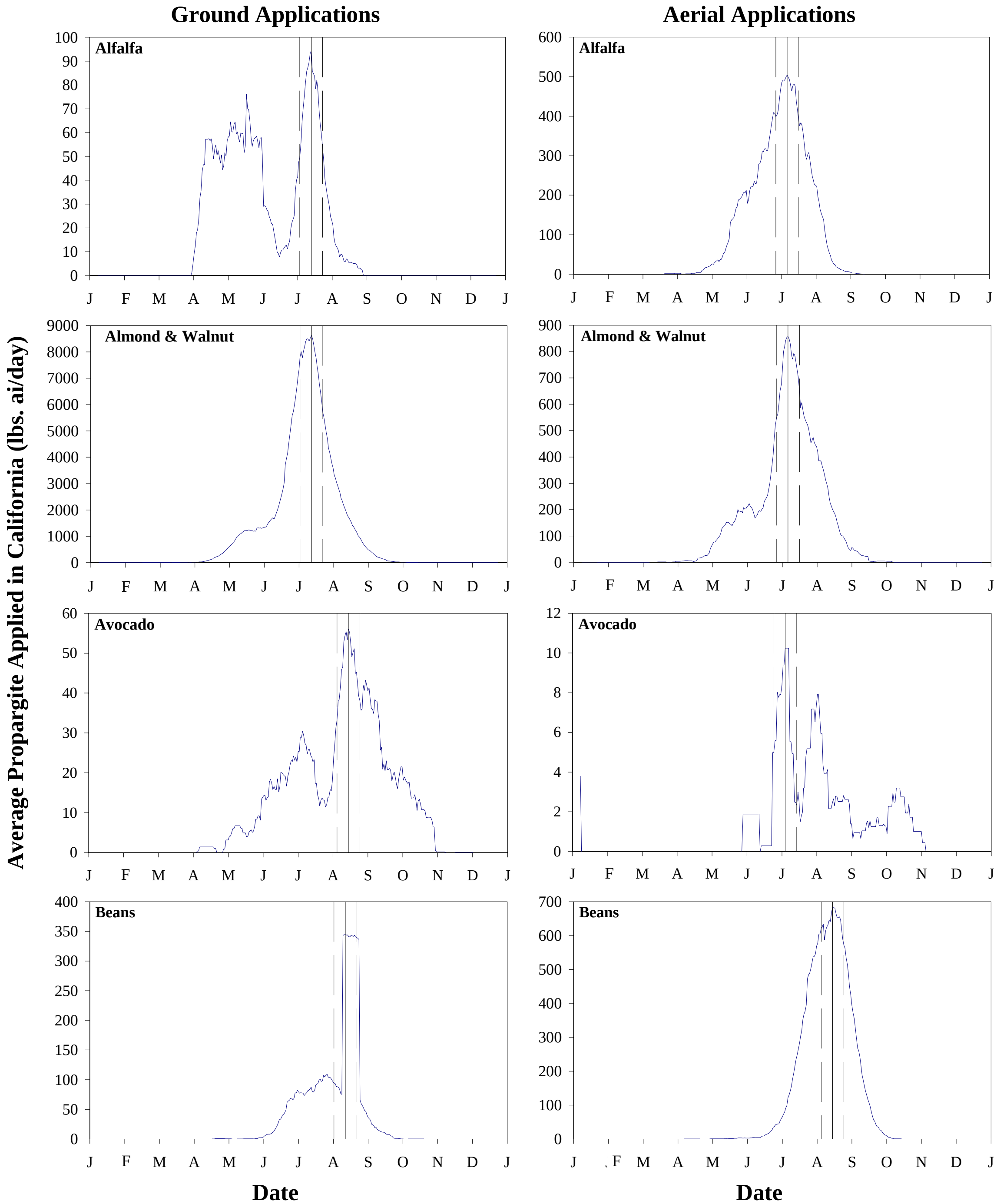
Two different sources of information were used to approximate the timing of propargite applications for each scenario. The maximum number of applications per growing season and minimum days before re-treatment with propargite were obtained from the Label Use Information System (LUIS) report produced by OPP, BEAD. Because some of the current labels do not provide this information, the maximum number of applications and minimum days before re-treatment provided on any of the labels listed for each exposure scenario were used (missing values excluded). Where no label relevant to the exposure scenario group provides this information, the applications per growing season and re-treatment interval were estimated using professional judgment (Appendix Table 1).

Appendix Table B2. Summary of scenario group information.

Scenario Group	Ground or Air Appl.	Appl. Rate (lbs. ai/A)	Number of Appl.	Appl. Interval	Max. Annual (lbs. ai/Yr)	1st – last Appl. Date	PRZM Scenario Name	Scenario Meteorological Station
1. Alfalfa	G	2.456	NS (2)	NS (21)	NS (4.912)	7/4 – 7/24	CA alfalfa OP	Fresno, CA (W93193)
	A	2.456	NS (2)	NS (21)	NS (4.912)	6/27 – 7/17		
2. Almond & Walnut	G	4	2	21	NS (8)	7/3 – 7/23	CA almond STD	Sacramento, CA (W23232)
	A	4	2	21	NS (8)	6/27 – 7/17		
3. Avocado	G	4.8	2	21	NS (9.6)	8/5 – 8/25	CA avocado RLF	San Diego County (W 23188)
4. Beans	G	2.456	2	21	NS (4.912)	8/2 – 8/22	CA row crop RLF	Monterey County, California (Santa Maria) (W23234)
	A	2.456	2	21	NS (4.912)	8/5 – 8/25		
5. Berries	G	1.92	2	21	NS (3.84)	NPUR (6/1)	CA wine grapes RLF	San Francisco, CA (W23234)
6. Citrus	G	3.36	2	28	5.76	4/23 – 5/20	CA citrus STD	Bakersfield, CA (W23155)
	A	2.456	2	28	4.094	10/20 – 11/16		
7. Clover	G	1.6375	NS (2)	NS (21)	NS (3.275)	6/18 – 7/8	CA alfalfa OP	Fresno, CA (W93193)
	A	1.6375	NS (2)	NS (21)	NS (3.275)	6/19 – 7/9		
8. Corn	G	2.625	1	--	2.625	7/3	CA corn OP	Sacramento, CA (W23232)
	A	2.625	1	--	2.625	7/14		
9. Cotton	G	2.456	2	21	NS (4.912)	6/28 – 7/18	CA cotton STD	Fresno, CA (W93193)
	A	2.456	2	21	NS (4.912)	7/23 – 8/12		
10. Forestry	G	2.4	3	NS (21)	NS (7.2)	6/7 – 7/2	CA forestry RLF	Arcata/Eureka, CA (W24283)
	A	2.4	3	NS (21)	NS (7.2)	6/7 – 7/2		
11. Grapes	G	2.88	2	21	NS (5.76)	7/3 – 7/23	CA wine grapes RLF	San Francisco, CA (W23234)
12. Hops	G	1.5	2	21	NS (3)	NPUR (6/1)	OR hops STD	Marion Co., OR (W24232)
13. Jojoba	G	1.6375	1	--	1.6375	NPUR (6/1)	CA cotton STD	Fresno, CA (W93193)
	A	1.6375	1	--	1.6375			
14. Mint	G	2.25	2	14	NS (4.5)	6/12 – 6/25	OR mint STD	Salem, OR (W24232)
	A	2.25	2	14	NS (4.5)	7/6 – 7/19		
15. Nectarine	G	2.88	2	21	NS (5.76)	7/3 – 7/23	CA fruit STD	Fresno, CA (W93193)
	A	2.88	2	21	NS (5.76)	5/22 – 6/11		
16. Ornamental Woody Shrubs & Vines	G	1.6	3	14	NS (4.8)	5/29 – 6/25	CA Nursery	San Diego, CA (W23188)
	A	1.6	3	14	NS (4.8)	7/1 – 7/28		
17. Other Ornamental	G	0.48	3	14	NS (1.44)	5/29 – 6/25	CA Nursery	San Diego, CA (W23188)
18. Peanuts	G	1.6375	2	14	NS (3.275)	7/25 – 8/7	CA row crop RLF	Monterey County, California (Santa Maria) (W23234)
	A	1.6375	2	14	NS (3.275)	8/10 – 8/23		
19. Sorghum	A	1.6375	1	--	1.6375	7/23	CA wheat RLF	Fresno, CA (W93193)

Scenario Group	Ground or Air Appl.	Appl. Rate (lbs. ai/A)	Number of Appl.	Appl. Interval	Max. Annual (lbs. ai/Yr)	1st – last Appl. Date	PRZM Scenario Name	Scenario Meteorological Station
20. Strawberry	G	1.92	2	21	NS (3.84)	11/20 – 12/10	CA strawberry (non plastic) RLF	San Francisco, CA (W23234)
21. Tree fruit	G	1.92	2	21	NS (3.84)	7/3 – 7/23	CA fruit STD	Fresno, CA (W93193)
22. Tree nut	G	1.92	2	21	NS (3.84)	5/20 – 6/9	CA almond STD	Sacramento, CA (W23232)

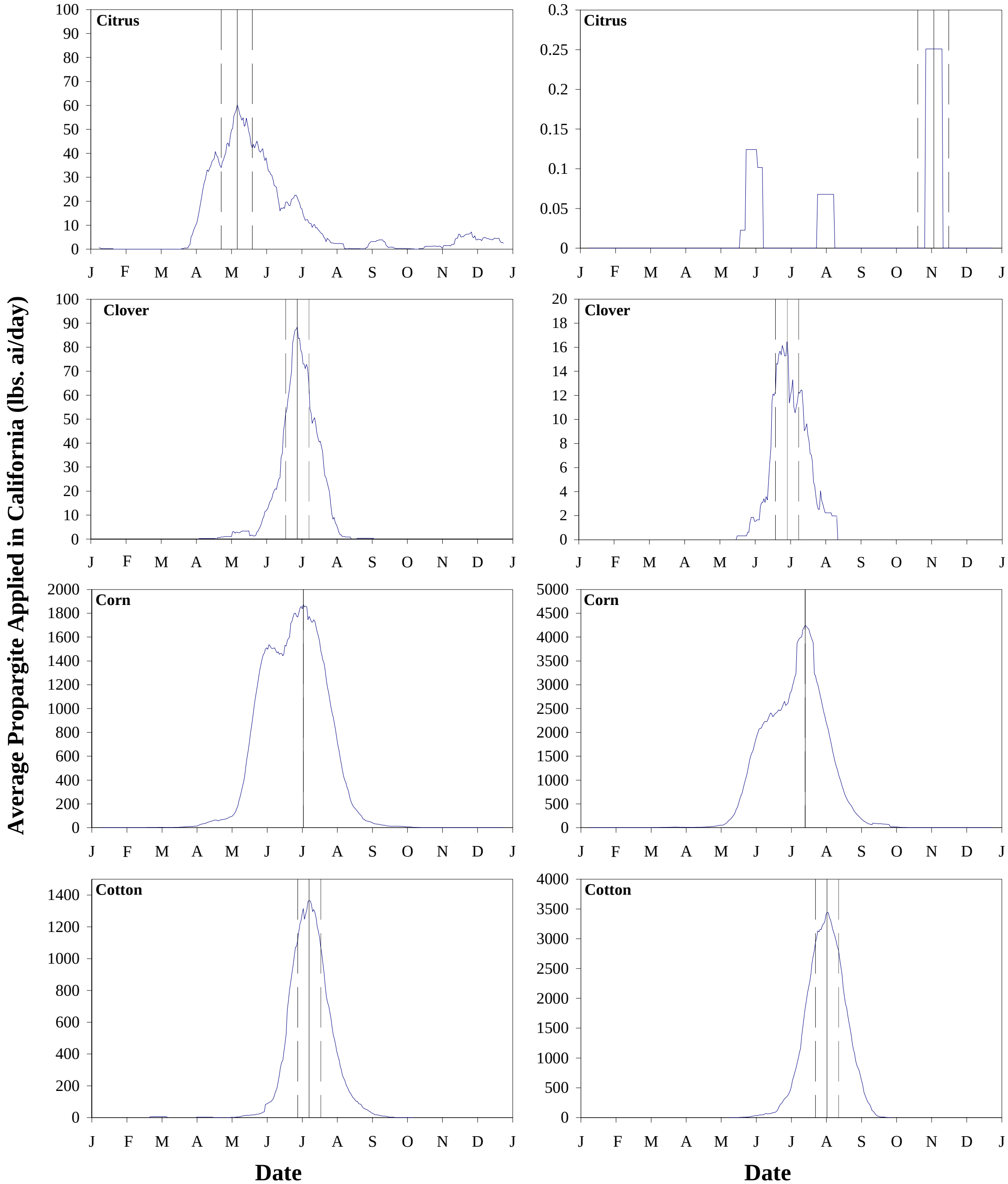
Application dates for each crop/site were derived from the CDPR PUR data set. Figure 2 shows a 16-day moving average calculated across all 17 years (1990 – 2006) of CDPR PUR data. (This can be thought of as the *average* of the moving-averages for all years in Appendix Figure 1.) The peak of the right graph is used to calculate the midpoint of the propargite application period used in each PRZM scenario. Using this peak value and the applications per growing season and re-treatment intervals from Appendix Table 1, the first and last scenario application days (dashed lines in Figure 2) are calculated to bracket the peak of the propargite application for each exposure scenario group.



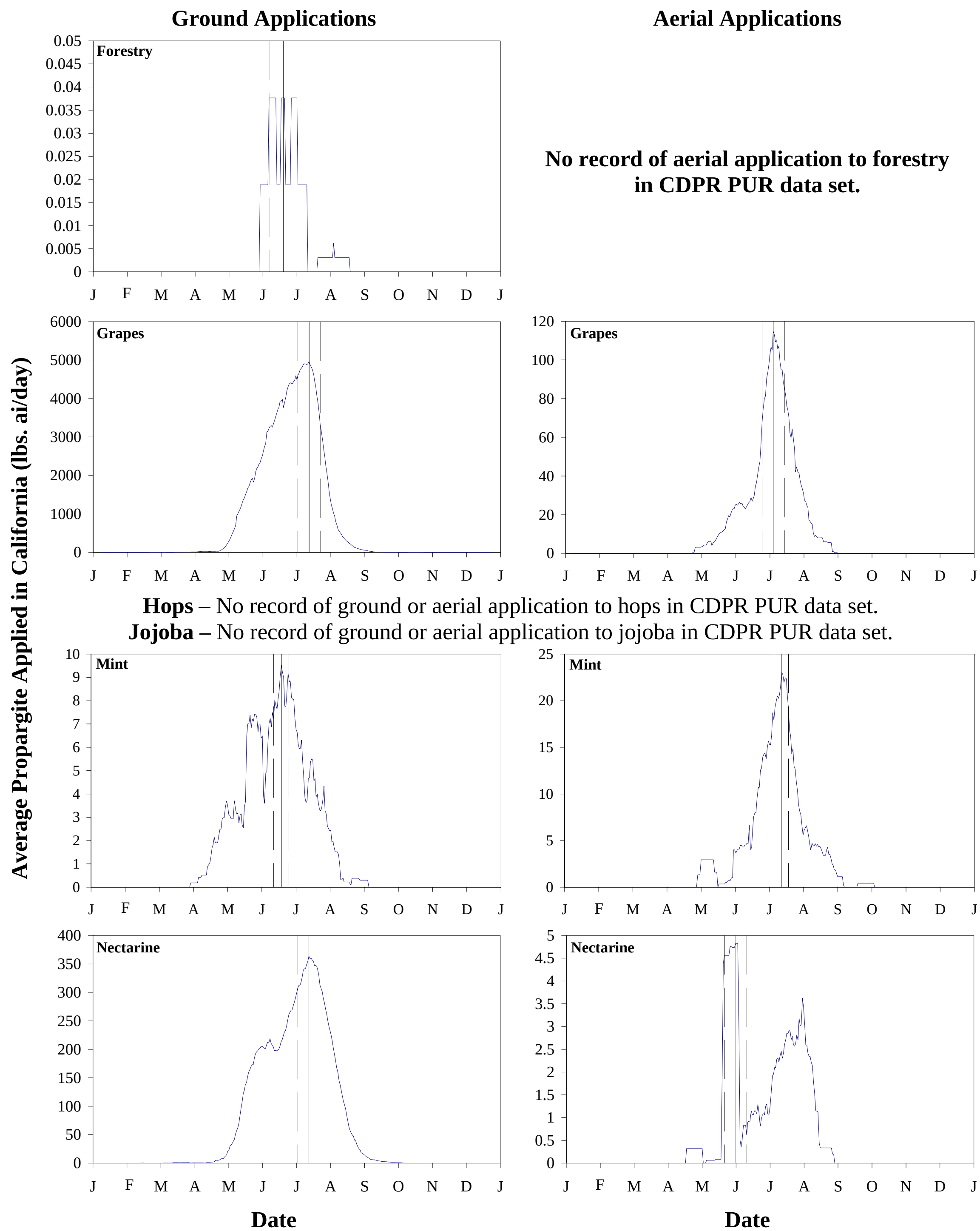
Appendix Figure B3. Generalized within-year propargite application by crop use according to the CDPR PUR data. Vertical lines indicate the date of propargite application in the single application scenarios (solid line) and first to last applications in the multiple application scenarios (dashed lines).

Ground Applications **Aerial Applications**

Berries – No record of ground or aerial application to berries in CDPR PUR data set.



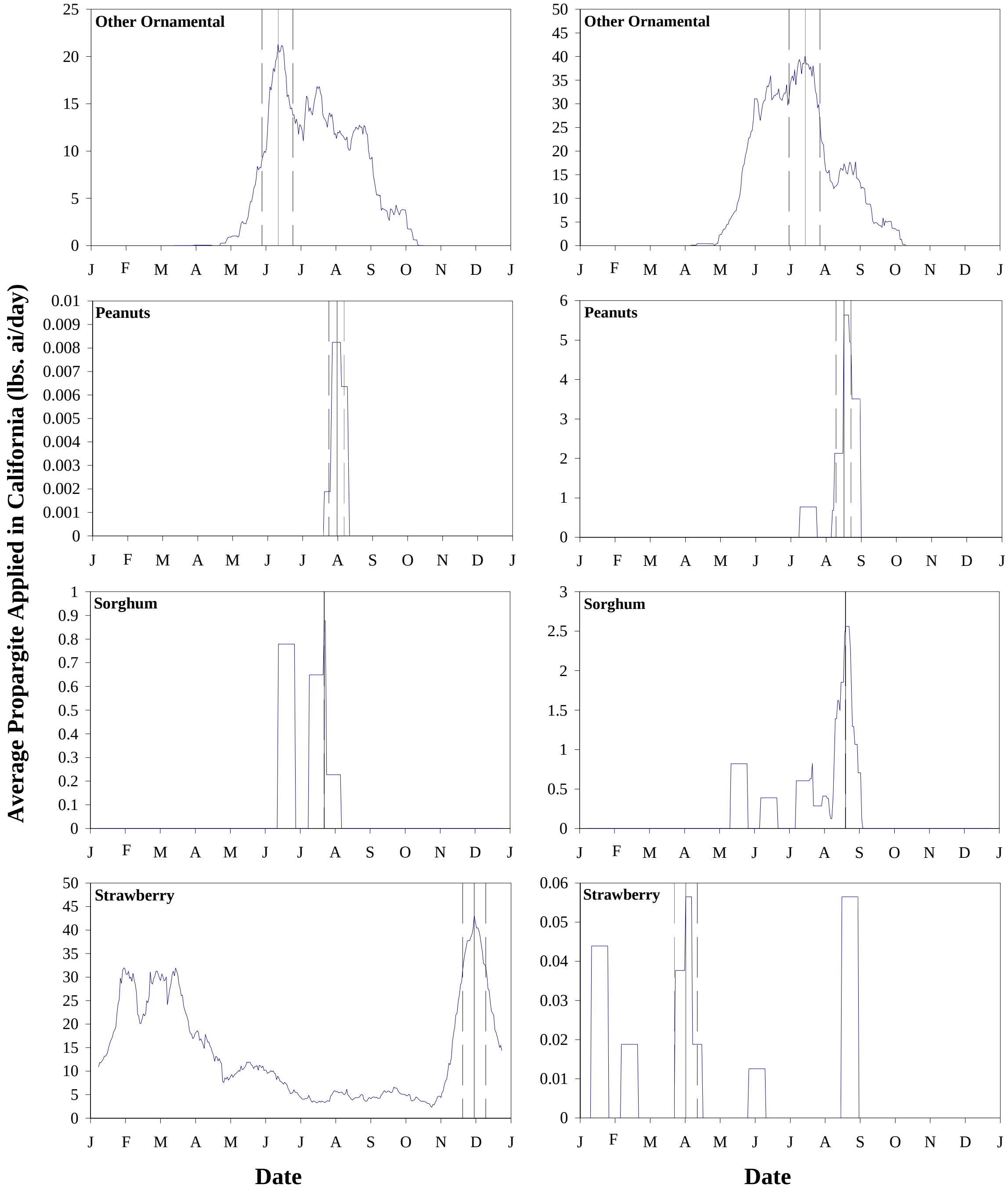
Appendix Figure B3. Continued.



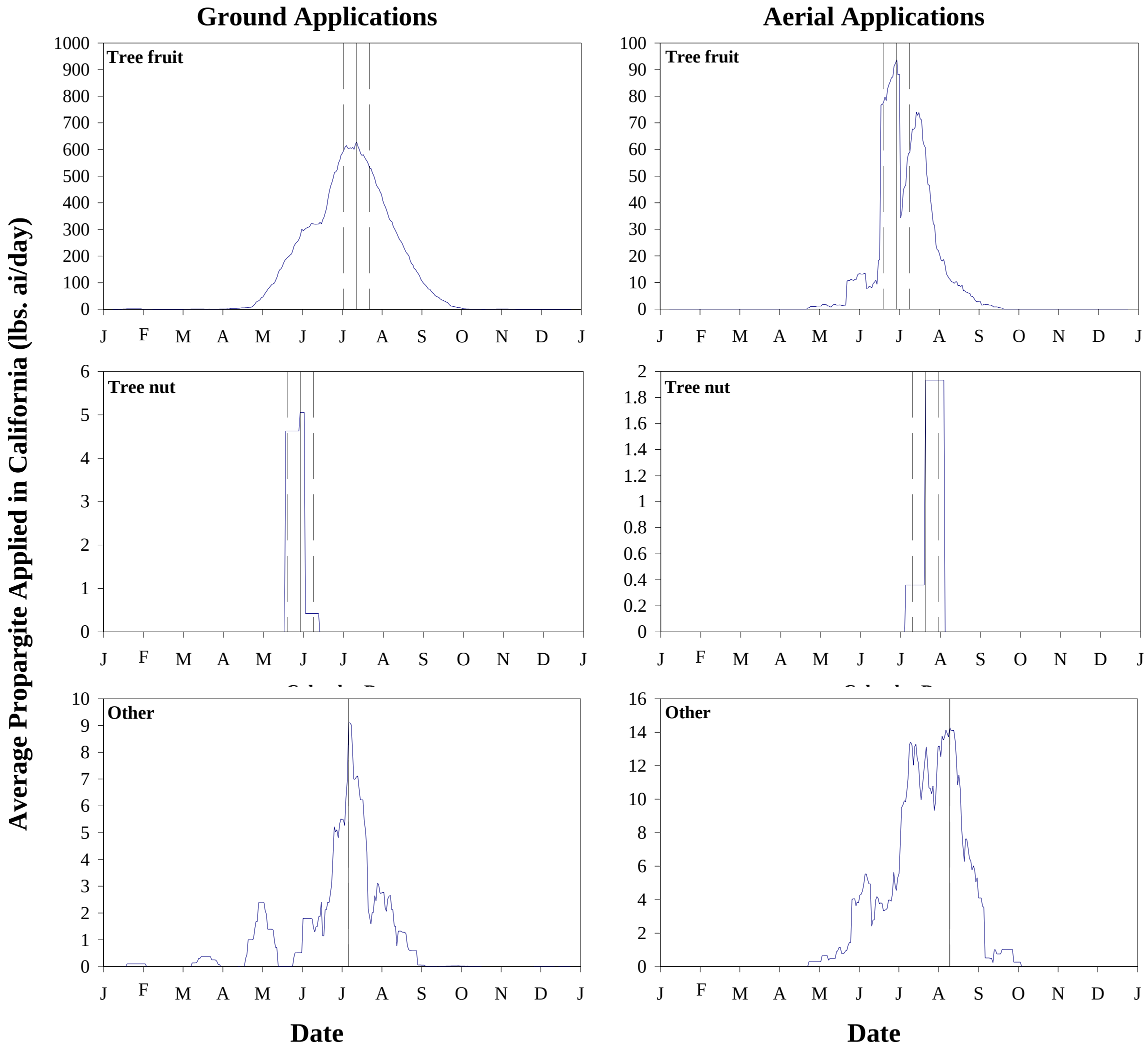
Appendix Figure B3. Continued.

Ground Applications **Aerial Applications**

Ornamental Woody Shrubs and Vines – No record of ground or aerial application to ornamental woody shrubs and vines in CDPR PUR data set.



Appendix Figure B3. Continued.



Appendix Figure B3. Continued.